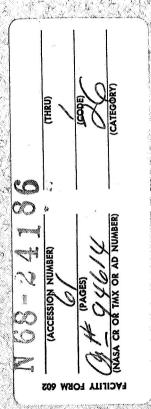
PHOTOELECTRIC YIELDS OF METALS IN THE VACUUM ULTRAVIOLET

R. B. CAIRNS

J. A. R. SAMSON





FINAL REPORT CONTRACT NO. NAS5-3918



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November 1966

GCA CORPORATION
GCA TECHNOLOGY DIVISION
Bedford, Massachusetts

Prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
GODDARD SPACE FLIGHT CENTER
Greenbelt, Maryland

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PHOTOELECTRIC YIELDS OF METALS IN THE VACUUM ULTRAVIOLET

by J. A. R. Samson and R. B. Cairns

GCA CORPORATION
GCA TECHNOLOGY DIVISION
Bedford, Massachusetts

SUMMARY

The object of this study was to measure the absolute photoelectric yield of various cathodes including W, Ni, A ℓ , Pt, LiF, and SrF $_2$ from 250 to 1300 Å. Also, the reproducibility of these yields were to be investigated periodically and conclusions to be drawn about their stability. The effects of irradiation by 1 MeV electrons on the yield of LiF was investigated. The photoelectric yields of three compounds, namely, CuBe, SrF $_2$, and LiF are tabulated in this report. The conditions under which enhanced yields can be obtained and the stability of the yields are discussed.

INTRODUCTION

The present final report summarizes the discussions of the previous quarterly reports and includes complete details of the results obtained during the eighth and final quarterly contract period.

The discussion is centered around four main topics, namely, (1) the stability of the photoelectric yield of a metal cathode and the similarity in yield from one sample to another, (2) techniques to enhance the photoelectric yields, (3) the photoelectric yields of thin insulating films of LiF and SrF_2 and the effect of Beta-ray bombardment on their yield, and (4) a tabulation of the measured photoelectric yields of the following three compounds: CuBe, SrF_2 , and LiF. The yields of 16 selected elements have been presented in a previously published report (GCA TR 65-29-N).

The work performed under this contract has resulted in the publication of three papers in accredited scientific journals and a GCA Technical Report as follows:

Title and Author(s)

Photoelectric Yield of Aluminum from 300 to 1300 Å (J. A. R. Samson and R. B. Cairns)

Rev. Sci. Instr. 36, 19 (1965)

Enhanced Photoelectric Emission between 200 and 1300 Å (J. A. R. Samson and R. B. Cairns)

Rev. Sci. Instr. 37, 338 (1966)

Metal Photocathodes as Secondary Standards for Absolute Light Intensity Measurements in the Vacuum Ultraviolet (R. B. Cairns and J. A. R. Samson) J. Opt. Soc. Am. (to be published)

Photoelectric Yields of Metals in the Vacuum Ultraviolet (R. B. Cairns and J. A. R. Samson)

GCA Technical Report No. 65-29-N

Duplicate copies of the journal articles are included at the conclusion of the report as the most direct means of presenting a complete picture of the results obtained during the present program.

DISCUSSION

Stability of Photoelectric Yield

The metal cathodes studied were all highly polished and made from standard available stock and were all precleaned with methyl alcohol prior to any measurements. The fact that the photoelectric yields of all the metals studied were quite similar assures the probability that the yield of a sample of a given element will be similar to the yield of a different sample of the same element. Quantitative data on three samples of tungsten are shown in Figure 1. These samples are actual cathodes used in the Bendix M306 electron multiplier as required by the Goddard Space Flight Center in their solar satellite program. From the figure, it can be seen that the maximum deviation from an average yield is only \pm 11 percent. These cathodes were later subjected to contamination and then recleaned. The yields were reproducible within a few percent.

A complete literature survey of the available photoelectric yield measurements was performed. Combining these data with the present ones, a composite yield curve could be obtained, whereby all measurements at a given wavelength lay within \pm 30 percent of the composite curve. This material has been discussed in detail in the seventh quarterly report and is the basis for a paper to appear in the Journal of the Optical Society of America.

Enhanced Photoelectric Yields

It has been discovered that the efficiency of photons to eject electrons from a metal increases with the angle of incidence of the bombarding photons. However, the number of photons reflected from the metal surface also increases. Thus, it is necessary to reuse these reflected photons if an enhanced yield is to be achieved. Studies of the yields at grazing incidence were conducted, and it was found that the enhanced yield was wavelength dependent - the enhancement being greater at shorter wavelengths. A practical cathode in the form of a polygon was successfully constructed which gave an enhanced signal of a factor of 5.5 at 200 Å and only 40 percent at wavelengths between 800 and 1300 Å. A photograph of the polygon is shown in Figure 2, and the effective photoelectric yield of its aluminum cathodes are shown in Figure 3 along with the yield of a single aluminum cathode.

Photoelectric Yield of Insulators

The photoelectric yields of thin films of LiF and $\rm SrF_2$ were measured between 200 to 1500 Å. The fluorides were evaporated onto polished metal substrates. Film thicknesses were typically several thousand angstroms. When the film thickness was too great, saturation effects were readily observed with photon intensities of the order of $\rm 10^9$ photons/sec/cm². With a 4000 Å thick film, no saturation was observed up to irradiation intensities of $\rm 10^{10}$ photons/sec/cm².

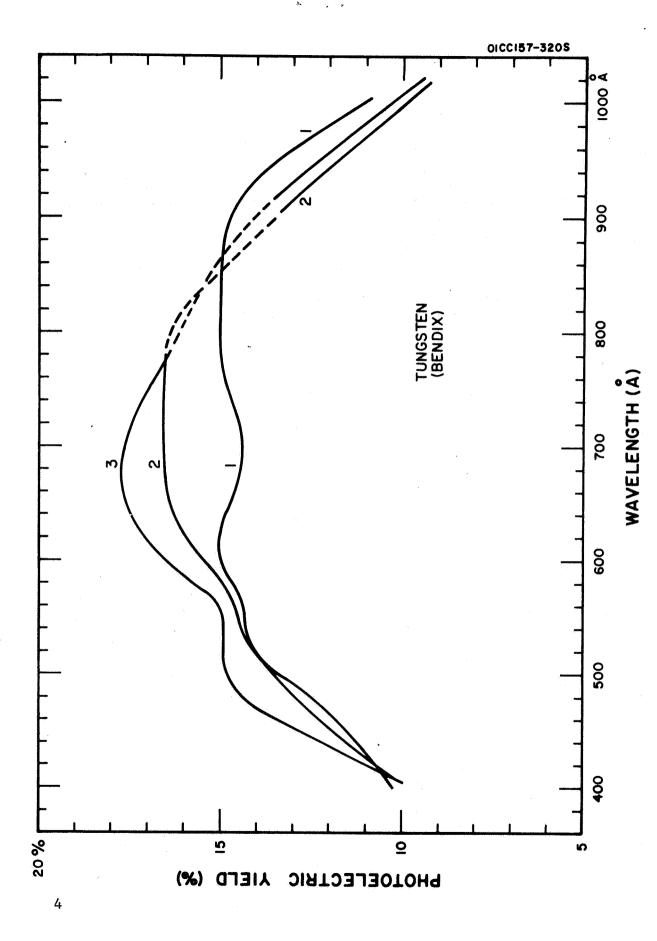


Figure 1. Photoelectric yield of tungsten.

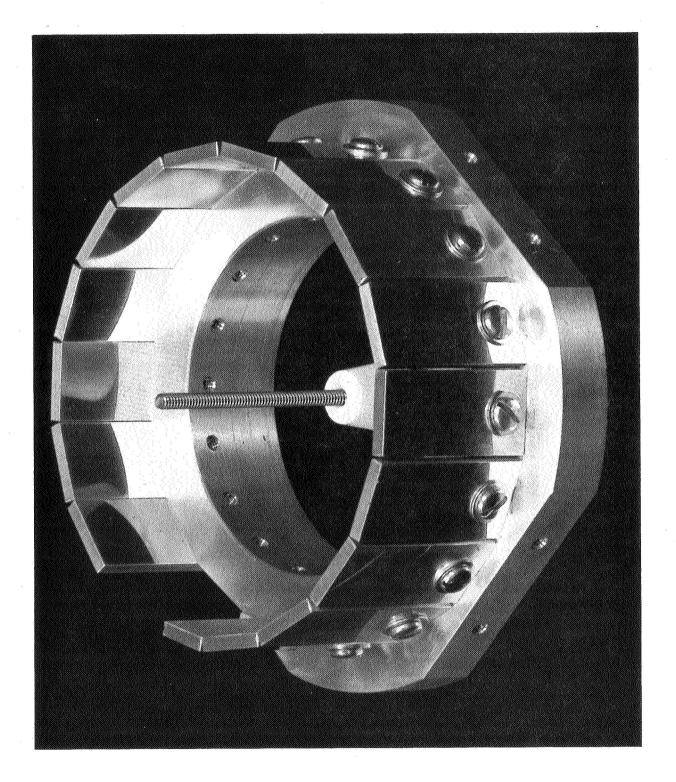
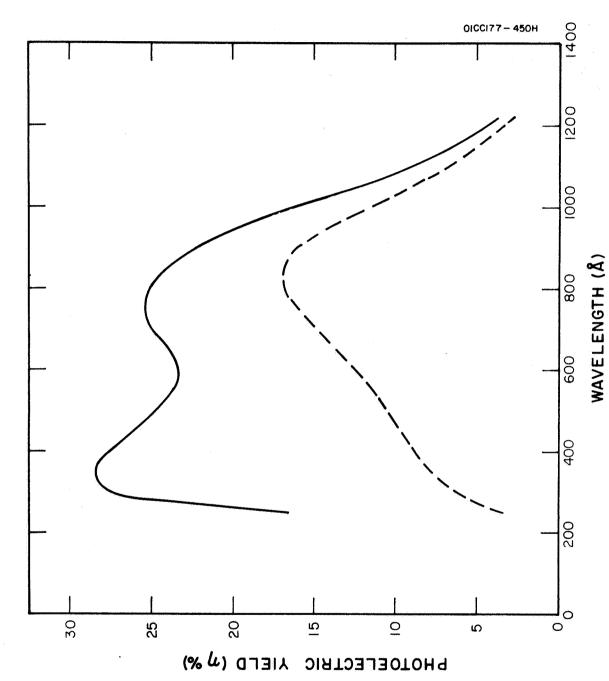


Figure 2. An eighteen sided polygon constructed from aluminum.



The photoelectric yield of a polygon cathode (solid line) and a single plate at normal incidence (broken line) measured as a function of wavelength. Figure 3.

The photoelectric yield of LiF and SrF, are shown in Figures 4 and 5, respectively. The actual magnitude of these yields vary with different samples perhaps due to thickness or rate of evaporation; however, the shapes of the curves are relatively constant.

LiF was subjected to a beta-ray flux from strontium 90-yttrium 90. The source contained approximately 15 millicuries of strontium 90 placed at a distance of 5.7 cm from the LiF sample. The sample was bonbarded by a total of 10^8 beta particles of 0.93 MeV energy. There was no change in the yield of this sample after irradiation.

Photoelectric Yields of CuBe, SrF2, and LiF.

The photoelectric yields of the cathodes studied during the final contract period are tabulated in Table 1.

CONCLUSIONS

The photoelectric yield of a metal is stable and can be used to determine the absolute intensity of vacuum ultraviolet radiation. The yield varies as a function of the angle of incidence; thus care must be exercised when absolute intensities are being measured.

An enhancement in the photoelectric yield of up to 5.5 can be realized at 200 Å, when radiation is incident at 80° on an eighteen-sided polygon. Greater enhancements are expected for more grazing angles of incident and at shorter wavelengths.

The use of LiF or SrF₂ cathodes also gives an enhanced photoelectric yield. However, a calibration of these cathodes may not remain constant due to contamination of their surfaces (for example, by water vapor). No deterioration was noticed when the samples were irradiated by 10^8 electrons of 1 MeV energy.

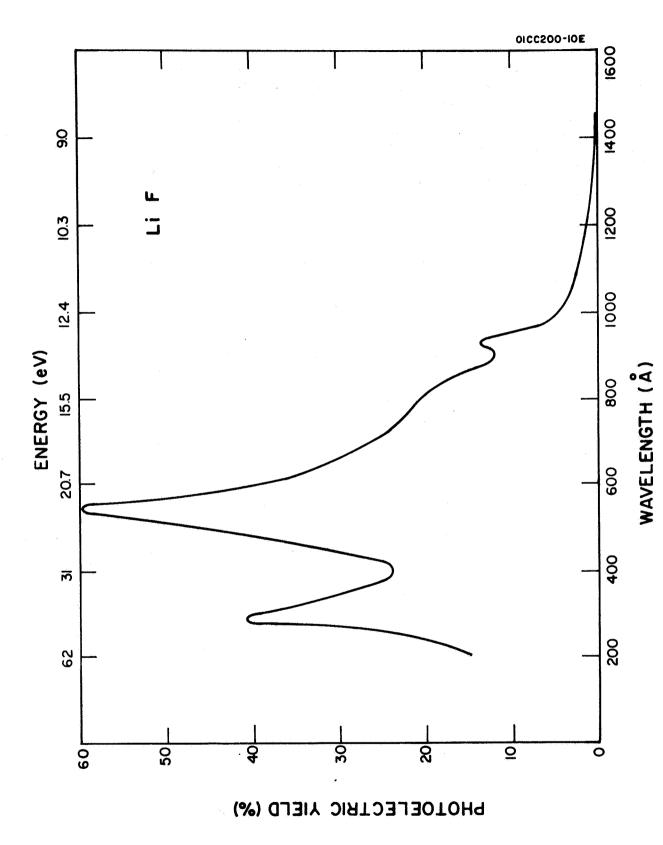
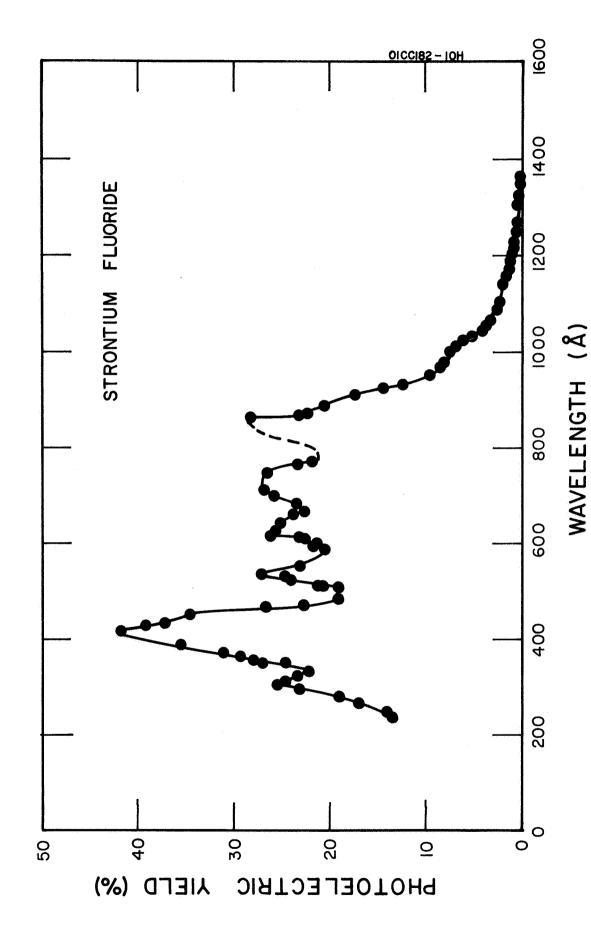


Figure 4. Photoelectric yield of lithium fluoride between 1400 and 200Å.



9

Figure 5. Photoelectric yield of strobtium fluoride between 1400 and 200A.

TABLE 1
PHOTOELECTRIC YIELDS OF VARIOUS CATHODES

2440 - 18.2 13.5 248 3.6 20.1 14.0 266 4.1 23.8 17.1 280 5.7 40.5 19.0 298 6.6 - 23.3 300 - - - 303 7.6 41.4 25.5 3815 - - 24.7 3223 8.3 34.1 23.5 3835 9.4 32.6 22.4 345 9.6 25.8 24.7 352 9.8 27.5 - 358 9.9 26.3 28.0 360 - - 27.3 363 10.3 26.2 29.5 388 10.1 23.4 35.9 399 - 22.4 - 428 11.6 23.9 39.3 4428 11.6 23.9 39.3 452 14.2 27.4 34.8 464 13.7 26.8 26.8 <t< th=""><th colspan="2">Copper- βeryllium</th><th>Lithium Fluoride</th><th colspan="2">Strontium Fluoride</th></t<>	Copper- βeryllium		Lithium Fluoride	Strontium Fluoride	
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618 15.9 38.4 26.4					
627 - 25.9	618 627		38.4	26.4 25.9	

TABLE 1 - continued

•	Copper-	Lithium	Strontium	
λΆ	Beryllium	Fluoride	Fluoride	
631	17.0	37.2		
645	17.9	32.2	25.3	
660		÷	24.0	
662	· -	_	- · · -	
671	_	28.1	22.7	
686	17.8	30.3	23.6	
703	22.2	27.8	25.9	
714	23.0	24.6	27.3	
719	21.3	24.4		
748	16.0	22.0	26.8	
765	16.9	21.8	23.4	
772	-	-	·	
772	15.6	21.0	21.8	
775	<u>.</u>	_		
780	_	21.2	<u> </u>	
912	11.0	11.2	17.3	
924	10.2	13.3	14.4	
935		-	12.1	
955	8.7	10.0	9.5	
968	8.0	7.2	8.6	
	7.5	5.3	8.1	
978	7.5	J.J	7.4	
1002		_	6.8	
1014	5. 4	3.9	5.9	
1025	J•4 -	5.9	5.1	
1035		3.3	4.2	
1048	4.7	3.3	3.8	
1056	. -	2.9	3.4	
1066	4.0		2.7	
1090	3.4	2.3 2.1	2.4	
1107	-			
1116	2.8	1.9	2.3	
1127	-	-	2.3	
1145	2.3	1.5	2.1	
1160	2.1	1.3	1.7	
1175	2.0	1.2	1.3	
1189	1.8	1.0	1.0	
1205	1.5	0.87	0.88	
1216	1.3	0.82	0.84	
1238	1.0	0.68	0.66	
1253	0.88	0.47	0.55	
1269	-	0.40	0.44	
1293	-	. 	-	

TABLE 1 - continued

λΆ	Copper- Beryllium	Lithium Fluoride	Strontium Fluoride
1307	-	ing di kanggada ya makangan ya mpakanaka a sasayan ya masa a di ingi ini ini ingi ini ini ingi ini ini	0.25
1323	0.25	-	0.19
1334	-	0.20	0.17
1352	0.17	0.15	0.12
1362	_	0.14	0.11
1379	0.14	.=	0.07
1401	-	0.08	0.05
1435	0.04	0.06	0.03
1462	_	0.04	
1489	-	-	-
1494	0.02	-	-

METAL PHOTOCATHODES AS SECONDARY STANDARDS FOR ABSOLUTE LIGHT INTENSITY MEASUREMENTS IN THE VACUUM ULTRAVIOLET

bу

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ABSTRACT

The photoelectric yields of 16 metals have been measured over the wavelength range 1200 to 200 Å. Results obtained from different samples of the same metal are compared and the feasibility of using photocathodes of metal foil, as standardly available, in the measurement of absolute light intensities in the vacuum ultraviolet is discussed. It is concluded that untreated photocathodes can be used with a probable uncertainty of about \pm 30 percent in the wavelength range 1100 to 400 Å. Changes in both the photoelectric yield and the reflectance of heated tungsten have been measured. Finally, some comments are made concerning the surface and volume photoelectric effects.

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INTRODUCTION

Many experiments in the vacuum ultraviolet require measurements of the absolute intensity of radiation. Various techniques have been devised to measure absolute intensities which employ thermocouples, ionization chambers, etc. These techniques, although accurate, cannot be incorporated simply into certain experimental designs. Thus, there remains a need for a secondary standard which is simple in operation, small in size, and which can be introduced into apparatus without radical modifications.

Metal photocathodes have been used as detectors of vacuum ultraviolet radiation in a number of experiments. They have the advantage when used in this wavelength region that they are insensitive to stray visible radiation. However, there have been reports in the literature of large changes in the photoyields of metals which have been either exposed to different gases or heat treated (see, for example, the work of Wainfan, et al.) [1]*. Thus, while a metal photocathode can be used to detect radiation, its use as an absolute intensity detector could be questioned.

This paper discusses the applicability of a metal detector for the measurement of absolute intensities. The yields of many metal samples have been measured under a variety of conditions and over a larger wavelength range than previously reported. Except where specifically stated, no attempt has been made to obtain outgassed metals of the highest purity and surface cleanliness. Thus, the photoelectric yields presented in this paper are not those of pure metals without surface contaminant layers, but are those of standardly available samples, having a stated bulk purity exceeding 99.5 percent, which have undergone a routine polishing and cleaning with methyl alcohol. It is the reproducibility of the yield and not its significance in terms of the band structures of the metals which is of prime interest in this work.

In what wavelength region, if any, would the photoelectric yield be insensitive to surface conditions? Early measurements near the photoelectric threshold showed the yield to be sensitive to surface cleanliness and work function [2]. This is to be expected since, in a region where excited electrons have an energy only slightly in excess of that required for release, small changes in work function will radically alter the yield. However, at wavelengths shorter than 1100 Å, electrons are excited to energies sufficiently large that small changes in work function will not so seriously affect the yield. If the photoelectric yield is defined as the number of electrons released from the metal per incident photon, it will clearly depend upon the reflectance of the metal surface since photons reflected cannot contribute to the electron emission. Thus, spectral regions where the reflectance is high yet dependent upon the surface condition will not have a stable photoelectric yield. In regions where the reflectance is low, however, changes in reflectance will not substantially alter the yield. For most metals, the reflectance

^{*} All numbers in [] represent reference numbers.

decreases in the vicinity of 1100 Å; for example, see Hass, <u>et al</u>. [3]. It is not surprising, therefore, that the photoelectric yield has been found to be relatively constant below 1100 Å but to vary considerably near the threshold.

It should be mentioned that this conclusion does not necessitate the assumption that a volume photoelectric effect, [4 through 7] which can be separated from the surface effect and is stable, exists and has a threshold near 1100 Å.

EXPERIMENTAL

The photoelectric yields of 16 metals have been measured over the wavelength range 1216 to 200 A and, where possible, have been compared with previously published data to establish reproducibility. To determine the yield, the number of electrons emitted from the metal photocathode must be measured and divided by the number of photons incident upon that surface. The experimental arrangement is shown in Figure 1. The absolute light intensity was measured at wavelengths shorter than $1022\ \text{\AA}$ (the photoionization threshold of xenon) using an ion chamber in the manner described by Samson [8]. At longer wavelengths, the ion chamber could not be used and absolute intensities were measured using a calibrated sodium salicylate coated photomultiplier. usual assumption was made that sodium salicylate has a constant quantum efficiency within the range 1216 to 1000 A. Some evidence indicates that this is not so and that the efficiency increases toward longer wavelengths [8]; however, any change in efficiency is unlikely to produce an error greater than 20 percent in the absolute calibration and will produce no error in relative measurements. The estimated accuracy of the yield measurements between 400 and 1000 Å was ± 8 percent, the error limits at 1250 Å were estimated to be + 20 percent and - 8 percent. Below 400 Å, the errors were approximately ± 20 percent due to the weakness of the incident radiation. In all measurements, the photon beam was incident normally upon the metal surface. When measuring the photoelectric current, the collector voltage must be sufficient to remove all electrons released from the cathode surface but must not accelerate these electrons to energies large enough to ionize residual gas in the than 10 torr and saturation currents should be obtained with a collector voltage of about 10V.

In Figure 2, the measured yields of tungsten are shown. Calibrations of two additional samples obtained from different stock were in good agreement. Also shown are the results of Hinteregger and Watanabe [9], Walker et al. [10], and Watanabe, et al. [11], who all used calibrated thermocouples for absolute intensity measurements. The estimated errors in the works of Weissler and Hinteregger are indicated. Successive calibrations by Watanabe gave good reproducibility (± 10 percent) at wavelengths shorter than 1350 Å. Additional measurements have been reported by Wheaton [12]. All calibrations in the 1100 to 400 Å region give similar yields. At wavelengths longer than 1100 Å, there is poorer agreement. For example, at 1026 Å, Watanabe obtained a yield of 9 percent, which is in good agreement with the present value of 8.7 percent.

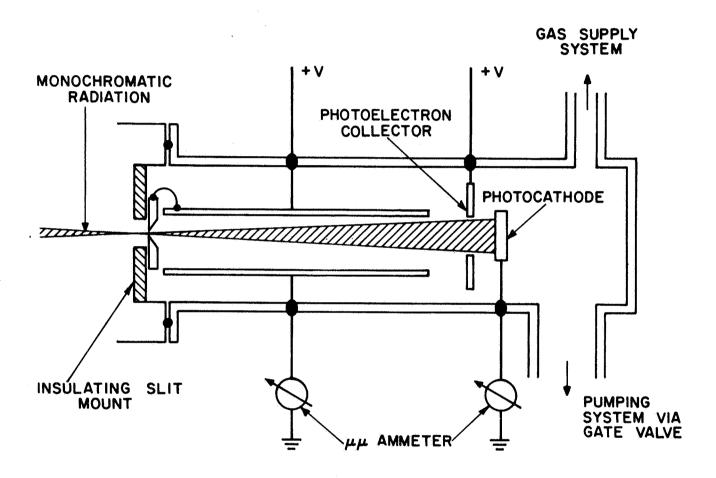


Figure 1. Diagram of apparatus used in the measurement of the photoelectric yield at wavelengths shorter than 1022A.

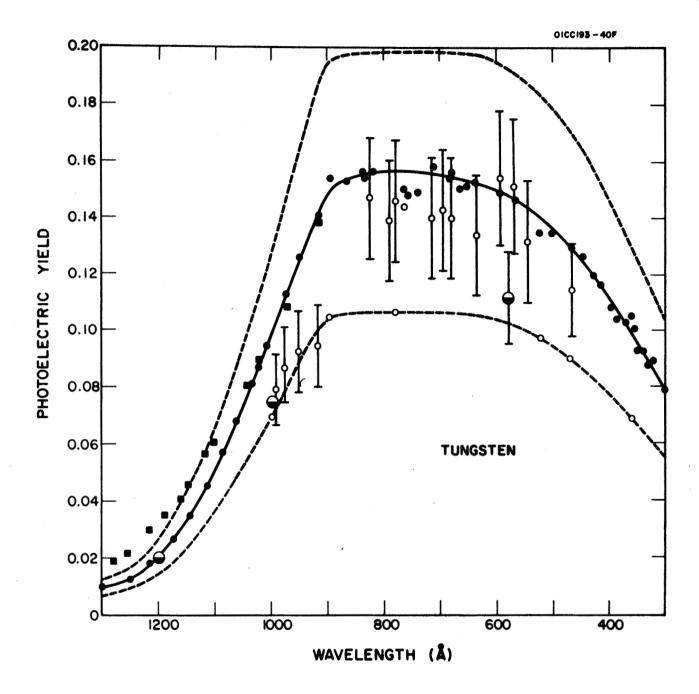


Figure 2. The photoelectric yield of tungsten

present data, O data of Walker, et al.,

data of Hinteregger and Watanabe,

data of Watanabe, et al.,

and ---- curves
representing the present data ± 30 percent.

At 1216 $\mbox{\normalfont{A}}$, however, Watanabe's value of 3 percent is approximately 60 percent higher than the present value.

The photoelectric yield of nickel is shown in Figure 3. Again, good agreement exists between present work and previous publications at wavelengths shorter than $1100~\text{\AA}$.

The yields of $A\ell$, Zn, Cu, Be, Fe, Ti, Ta, In, Pt, Sn, Mo, Ag, Au, and Pb are shown in Figures 4 through 8. For the sake of clarity, the experimental points have not been included. The smooth curves represent averages of the data which show a spread similar to that indicated in Figures 2 and 3. The metal samples were 0.005-inch thick foils obtained from A. D. Mackay, Inc. The photoelectric currents from these samples were measured soon after the metals had been exposed to the rare gases, He, A or Xe, used in the ion chamber. These different gases did not alter the yields nor did exposure to air at atmospheric pressure. This agreed with earlier reports.

To examine the effect of prolonged exposure to a low pressure environment, the yield of silver at 584 Å was repeatedly measured over a period of 50 hours, during which the pressure was maintained at 10^{-5} torr. Eight measurements were made, the yields being 0.091, 0.090, 0.091, 0.088, 0.087, 0.088, and 0.087, i.e., allowing for experimental error the yields remained constant. At a pressure of 10^{-5} torr, a monolayer of gas collects on a surface in less than one second and so the sample could not be considered free from absorbed or adsorbed gases.

The surface composition and smoothness of a metal photocathode affect its reflectance and, hence, its yield. However, at wavelengths shorter than 1100 Å, the reflectance is sufficiently low that the yield is not greatly changed by small differences in surface features. Extreme roughness will alter the yield [13]. Photoelectrons released by radiation which penetrates the interstices of the roughened surface might be recaptured by the metal thus reducing the yeild. In addition, light incident upon the roughened surface can no longer be regarded as striking the surface normally. Oblique incidence increases the yield [13,14]. Thus, the different samples can be expected to have similar yields only if their surfaces are smooth and polished. A mirror-like finish is, however, not essential.

Finally, it should be mentioned that since all the measurements were made at normal incidence, the yields reported are independent of the degree of polarization of the incident radiation.

It is concluded that smooth surfaced pure metal untreated photocathodes (which are sufficiently thick so as not to transmit radiation) can be used in conjunction with the data obtained in Figures 2 through 8, to determine absolute intensities with an accuracy of about \pm 30 percent in the wavelength region 1100 to 400 Å.

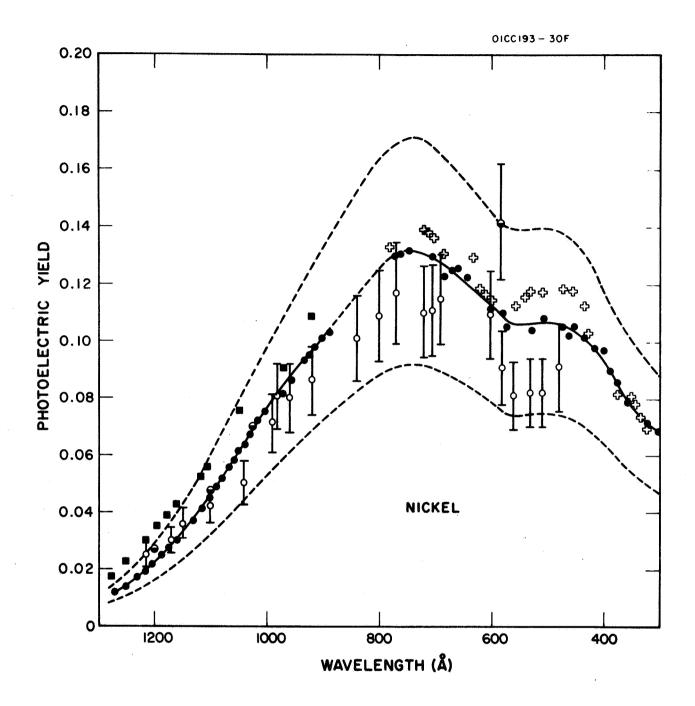


Figure 3. The photoelectric yeild of nickel

present data, present data (former calibration), data of Hinteregger and Watanabe, data of Watanabe, et al., and ---- curves representing the present data ± 30 percent.

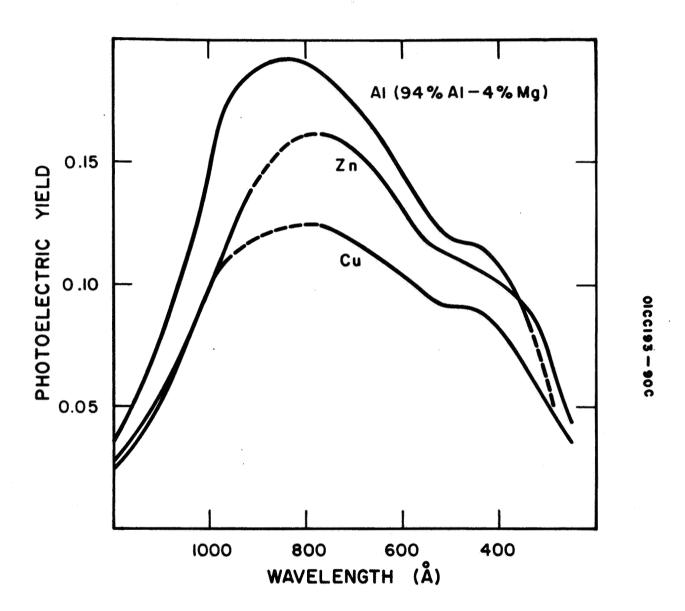


Figure 4. The photoelectric yields of $A \ell\text{-Mg}\text{, An,}$ and Cu.

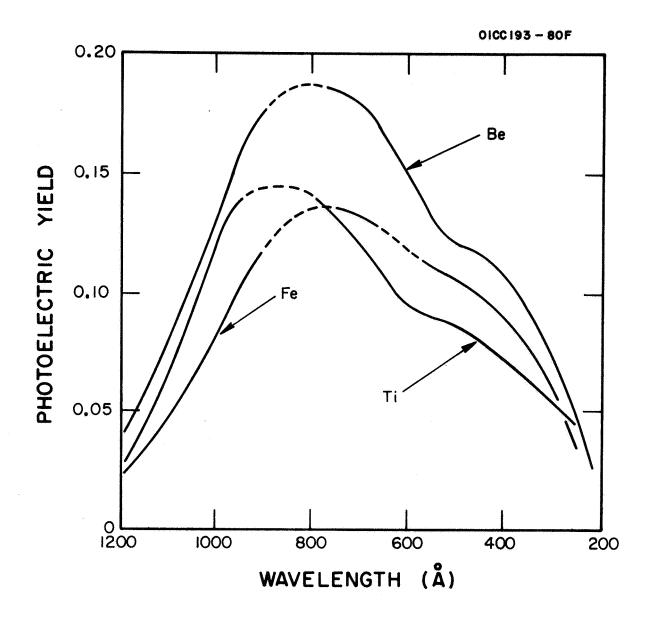


Figure 5. The photoelectric yields of Be, Fe, and Ti.

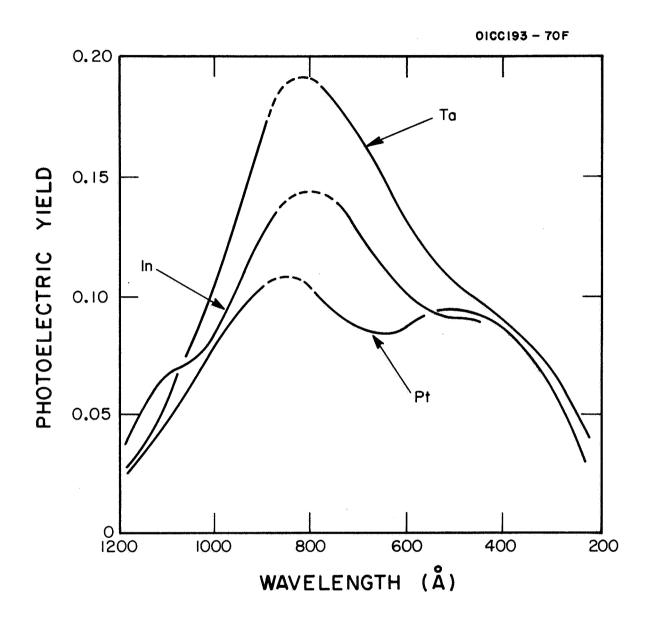


Figure 6. Photoelectric yields of Ta, In, and Pt.

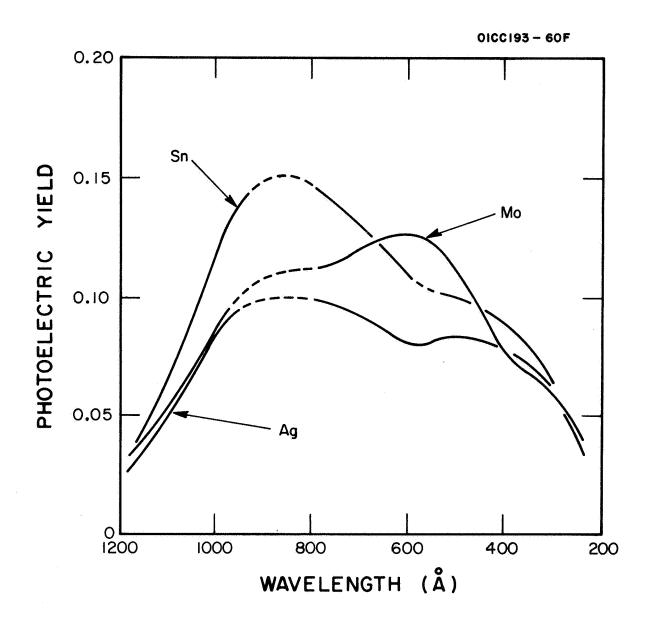


Figure 7. The photoelectric yields of Sn, Mo, and Ag.

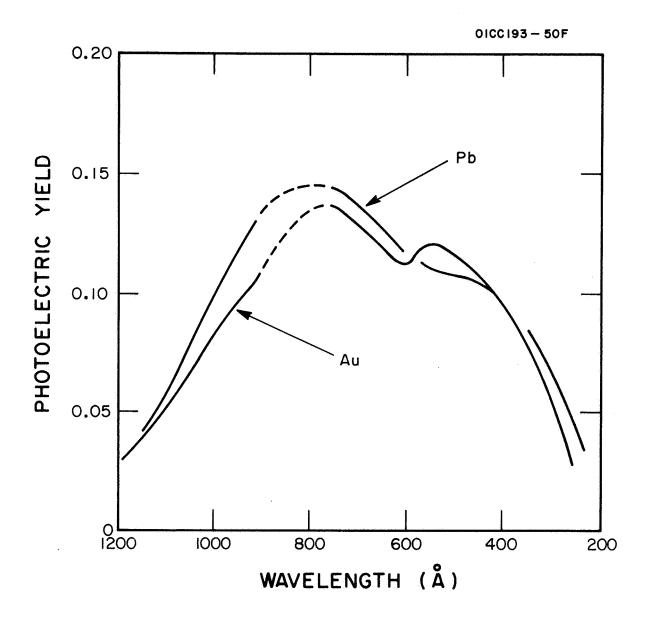


Figure 8. The photoelectric yields of Pb and Au.

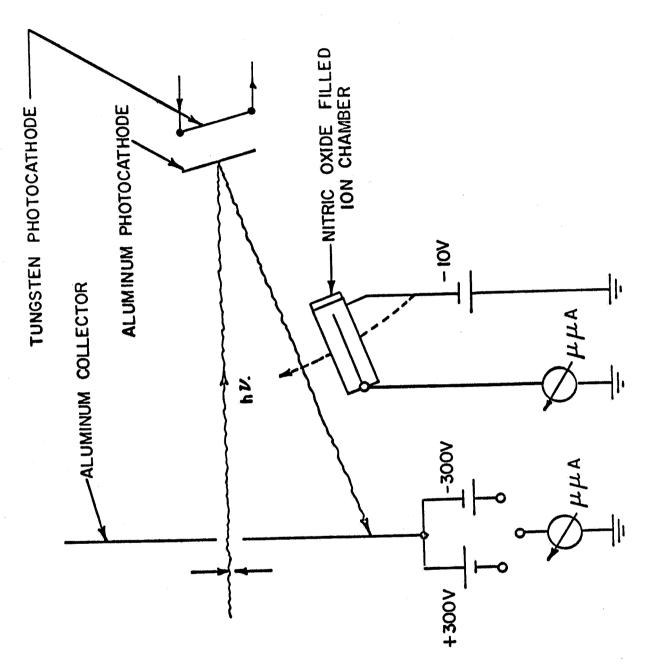
It will probably become possible to extend the 400 Å limit when more data of higher accuracy become available in this region. In the ensuing portion of this paper, certain effects are considered which alter the yield and which should, therefore, be avoided if use is to be made of the above data.

Certain Effects of Heat Treatment

The photoelectric yield has been shown to decrease over the wavelength range 1100 to 400 Å when the cathode is heated in vacuum [1]. This could be due to several effects: changes in surface contamination (either the removal of absorbed gases or the more rapid formation of oxides or baking on of contaminant layers) or changes in reflectance. An experiment has been made to determine whether the reflectance of an untreated sample changes during heat-Consider existing data for aluminum. The reflectance of pure aluminum deposited in an ultrahigh vacuum is 0.9 at 1216 Å [15], whereas for a sample deposited and then maintained in a vacuum of about 10^{-5} torr, it is 0.5 [16]. If, at a pressure of about 10^{-5} torr, heating were to remove all contaminants and as a result the reflectance of a sample were to increase from 0.5 to 0.9, this alone would account for a decrease in the photoelectric yield by a factor of five. In the following experiment, the reflectance and yield of a tungsten photocathode maintained at elevated temperatures were measured. The necessary apparatus is shown in Figure 9. A two-meter normal-incidence-vacuum spectrograph was used to illuminate at nearly normal incidence either an aluminum or tungsten photocathode with monochromatic 1216 Å radiation. The tungsten photocathode was 0.001-inch thick foil. An electric current, which was passed through the tungsten foil, could be adjusted to raise the temperature of the foil to any required value within the range 20 to 950°C. Temperatures above 820°C were measured using an optical pyrometer. The aluminum photocathode could be lowered out of the path of the light beam.

To measure the yield of the hot tungsten, the absolute intensity of the incident radiation and the resulting photoelectric current had to be known. To determine these quantities, an aluminum collector was held at a positive potential sufficiently high with respect to the aluminum or tungsten photocathodes to collect all photoelectrons. Thus, with the aluminum photocathode withdrawn from the light beam, the photoelectric current from the hot tungsten was measured. With the aluminum photocathode intercepting the beam, the photoelectric current from the aluminum was measured. The yield of the aluminum was known and hence the absolute intensity of the radiation could be calculated. Knowing the absolute intensity and the photoelectric current from the hot tungsten, the yield of the tungsten could be calculated. Reflected light striking the collector produced no error since any photoelectrons ejected were recollected. At the temperatures employed, the thermionic emission from the heated tungsten was negligible.

Relative values of the reflectance of the tungsten were measured at different temperatures using a nitric oxide filled ion chamber to monitor the light reflected from the heated foil. The ion chamber, having a lithium fluoride window, was insensitive to the continuous spectral emission from the



Experimental arrangement for the measurement of the yield and reflectance of heated tungsten. Figure 9.

TABLE I. The Photoelectric Yields and Reflectances of Tungsten at 1216 $\hbox{\begin{tabular}{l} A when at Different Temperatures \end{tabular}}$

Heating Current (Amps)	Temp. °C	Measured Yield η	Reflectance R	Yield $\gamma=\eta/(1-R)$
0	25 [°] C	.028	.25	.038
5		.029	.26	.039
10		.028	.27	.038
15		.025	.29	.035
20		.021	.32	.031
25		.015	.39	.024
30		.007	.46	.013
36		.006	.51	.012
40		.006	.51	.011
44	_	.006	.52	.012
50	950°C	.006	. 52	.013

glowing tungsten. These measurements were made absolute by determining the absolute reflectance of tungsten at room temperature. This was achieved by allowing the reflected light to strike the collector which was held at a negative potential. The resulting photoelectric current from the collector was Since the photoelectric yield of the aluminum collector was known, the absolute intensity of the reflected light and, hence, the reflectance of the heated tungsten could be calculated. With the collector at a negative potential, no electrons from the tungsten photocathode were collected. data obtained are listed in Table I. During outgassing, the reflectance increased and the yield decreased by factors of approximately two and five, respectively. Each quantity attained a constant value at high temperatures. These data have been used to calculate the number of electrons ejected per absorbed photon (γ) , i.e., the yield as previously defined (η) divided by (1-R), where R is the reflectance, The yield γ changed during heating. Thus, the dependence of the photoelectric emission on temperature cannot be ascribed solely to changes in reflectance. When cooled in vacuum, both R and η returned almost completely to their original values. It should be mentioned that during the cooling process, which was under vacuum and slow, gas layers would re-cover the surface and oxide layers could possibly be re-formed.

Newman and Oppenheimer [17] have reported that in the vacuum ultraviolet, the reflectances of platinum and gold foils do not change when heated. However, they took the precaution of preheating each foil "to eliminate any long time effects due to adsorption of gases."

Photocathodes used for absolute intensity measurements in systems which are not at an ultrahigh vacuum should not be heat treated.

DISCUSSION

The photoelectric yield η of all the calibrated photocathodes increases with decreasing wavelength in the region 1400 to 1000 X; see Figures 2 through This increase has been ascribed to the onset of a volume photoelectric effect. A variety of definitions of the volume effect appear in the literature. Initially, it was supposed that free electrons in the conduction band of a metal could not absorb radiation and as a result, photoemission was confined to electrons at the surface of the metal, which were subject to surface changes in electric potential. Later it was suggested that effects due to damping of electromagnetic waves within the metal could account for electron emission from the volume of the metal [4]. An additional mechanism for the volume effect was proposed by which electrons could be excited due to the fact that they exist in a periodic electric field within the metal. Fan [6] considered such an effect and concluded that it could not be neglected except in the immediate neighborhood of the photoelectric threshold. Hinteregger [7], whose measurements of Be showed a rapid increase in yield by about 9 eV, hypothesized the existence of a volume effect originating from electrons bound in an energy level about 9 eV below the vacuum level and having a high cross section for photoexcitation. Most recently, the surface photoelectric effect has been attributed to electrons excited from the conduction band of the metal and the volume effect to those excited from more tightly bound levels. A confusion

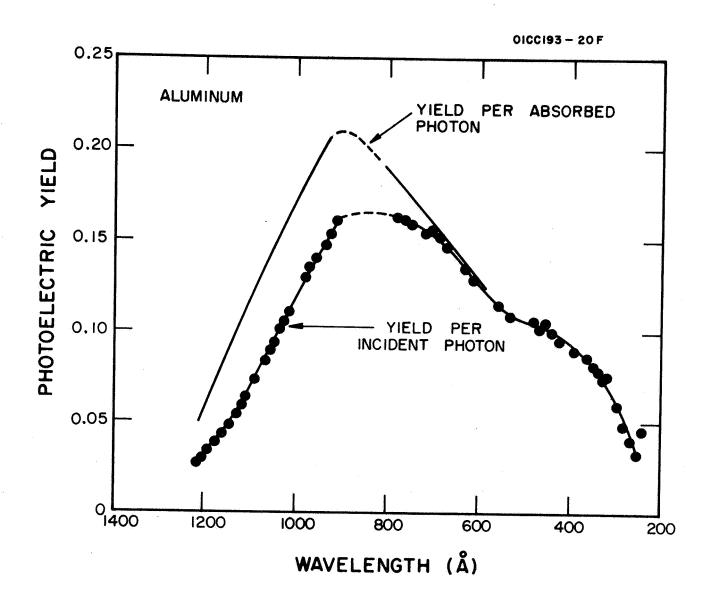


Figure 10. The photoelectric yield of aluminum.

exists. In certain cases, the volume effect has been thought to refer to the emission of conduction band electrons from the body of the metal, but in other cases, to the emission of electrons from inner atomic energy levels. The term surface effect has also been used to refer to the emission of electrons from the conduction band but more usually describes emission from the surface of the metal.

Consider the photoelectric yield of aluminum. For comparison with theory, the yield per absorbed photon γ and not the yield per incident photon η must be known. Both yields γ and η of aluminum are plotted as a function of wavelength in Figure 10, the data applying to untreated aluminum samples. The reflectance data, used in the calculation of γ , were those measured by Walker, et al.[16]. Both curves show a significant increase in yield in the 1200 to 900 Å region. This increase has been attributed to the volume photoelectric effect, having a threshold at about 9 eV. This is improbable for the following reasons. First, the total photoabsorption coefficient $\alpha_{\rm p}$ of aluminum is less than 2 x 10 6 cm $^{-1}$ throughout the entire energy range 1 to 100 eV, and as a result, more than 98 percent of all photons penetrate beyond the surface monolayer of the metal. There is no rapid change in $lpha_{T}$ close to the supposed onset of the volume effect. Secondly, the increase in yield is not likely to be due to the ejection of electrons bound in a discrete energy level approximately 9 eV below the vacuum level. In aluminum, the tightly bound inner electrons can be disregarded since more than 70 eV is required for their ejection. For electrons in the conduction band, it is convenient to divide the coefficient α_T into two parts; one, α_A , leading to transitions to states lying between the Fermi level and the vacuum level and the other, α_T - α_A , leading to transitions to states lying above the vacuum level. The photoyield γ will then be approximately proportional to 1 - $\alpha_{\rm A}/\alpha_{\rm T}$. If this factor alone is considered, the yield would increase if $\alpha_{\!A}/\alpha_{\!T}$ decreased, or since the coefficient $lpha_{
m T}$ does not increase if $lpha_{
m A}$ decreased. An appreciable reduction in $lpha_{
m A}$ is not expected since, in aluminum, interband transitions are significant only near 1.5 eV.

However, the yield depends not only on the initial electron excitation process but also on the probabilities of escape of the excited electrons. This consideration is included in a theory for the photoelectric effect given by Berglund and Spicer [18]. In this theory, no distinction is made between the mechanisms of emission from the surface and volume. It is assumed that photons are absorbed exponentially as they penetrate the metal, that the directions of motion of excited electrons are isotropic, that electrons, if scattered, are scattered isotropically, and that the transmission of electrons through the metal can be described by an exponential factor. Electrons reaching the surface must have a component of momentum normal to the surface which is greater than the work function of the metal. To obtain quantitative values of the yield (γ) , the work function (Φ) , the photoabsorption coefficient and the electron mean free path must be known, the latter two parameters as a function of energy. As the energy of the incident photons and, hence, the energy of the initially excited electrons increases, more electrons can escape. Consider the case of electrons having kinetic energy E. Then, if scattering is neglected, the fraction f of excited electrons which can escape is

given by 1/2 $\{1 - (\Phi/E)^{1/2}\}$. Assume Φ to equal 4.5 eV, then if E is 5 eV, f = 0.026, but if E is 10 eV, f = 0.164. These figures would be modified if electron scattering, including backscattering, is considered but there remains an increase in yield towards higher energies. In addition, when $E > 2\Phi$, inelastic collisions can make possible the ejection of two electrons per absorbed In the neighborhood of the plasma frequency w, both the photoabsorption coefficient and probably the electron mean free path [19] decrease with increasing energy. As a result, the yield at energies close to and exceeding Mo might be expected to be small. The measured photoelectric yields of metals do not show a significant decrease in the neighborhood of the plasma frequency. Indium is of interest since its plasma frequency occurs in a region where the yield is rapidly increasing, in the manner characteristic of all metals. present data agree with those of Watanabe [11] and are consistent with those of Axelrod [20] (who prepared indium under conditions of high vacuum) in showing a localized reduction of yield in the vicinity of the plasma frequency. However, the yield attains its maximum value at shorter wavelengths. the energy how is not the most significant parameter in determining the shape of the yield curve.

Discontinuities in the yields might be expected at other specific wavelengths. The transmittances of thin unbacked films of indium and tin have been shown by Walker, et al. [16] to decrease rapidly at wavelengths close to 750 and 510 Å. However, at these wavelengths, no discontinuities in the photoyields have been found. Walker, et al. suggested this this provided evidence for an absorption process which gives rise to no photoemission. Such an explanation requires the assumption that, in their experiment, the loss of photoelectrons due to photons absorbed in this process was equal to the loss due to photons transmitted at slightly longer wavelengths. This assumption could not be generally valid although it might hold for a thin film of a particulat thickness. For the thick metal sample of tin used in the present work, which was opaque at all wavelengths, a decrease in yield was expected to 510 Å. No such decrease was found. It is apparently necessary to take account of events subsequent to the initial absorption process which could lead to photoemission.

It has been mentioned that some present theories of the photoelectric effect assume that the directions of motion of both photoexcited and scattered electrons within the metal are isotropic. If this is so and if photons are absorbed exponentially as they penetrate the metal, then the ratio of the number of electrons ejected from the side of the metal upon which light is incident to the number ejected from the opposite side must always exceed unity. For the limiting cases of samples having semi-infinite and nearly zero thickness, this ratio would be \propto and 1, respectively. However, Rustgi, et al. [21] found this ratio to be less than 1 at wavelengths shorter than 750 Å. This suggests that the motion of excited electrons might be preferentially in the direction of the incident photon beam. Further experiments are required to clarify this point. The total photoelectric emission from transmitting films will be a function of their thickness, and so only opaque photocathodes should be used for absolute intensity measurements.

This discussion emphasizes the need for further measurements of the photoelectric yield in the vacuum ultraviolet. The effects of surface contaminant layers and absorbed gases should be studied together with determinations of the mean free paths and initial directions of motion of electrons excited within the metal. Many of these experiments must be performed under conditions of ultrahigh vacuum.

For work in the vacuum ultraviolet, the continued use of the terms surface and volume photoelectric effect seems inadvisable unless specific definitions are provided.

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PHOTOELECTRIC YIELD OF ALUMINUM FROM 300 TO 1300 Å

by

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ABSTRACT

The photoelectric yield of aluminum type 5086-H32 containing 94 percent A2 and 4 percent Mg has been measured at wavelengths between 300 and 1300 Å. At 584 Å the yield increased by 50 percent when the angle of incidence was changed from 0 to 50° . At 1026 Å, the yield remained nearly constant for such a rotation. In general, the yield was a function of the wavelength, the angle of incidence, and the degree of polarization of the incident radiation. The photoelectric yields were found to be stable and reproducible.

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INTRODUCTION

The use of metal cathodes is common in windowless electron multipliers; however, the photoelectric yields of such cathodes and their reproducibility are not well known.

The yields reported here for for the spectral region below 1300 Å, the region where the volume photoelectric effect is important. The yields of many metals have been measured in this region [1 through 4]. However, they have all been measured using thermopiles to determine the absolute intensity of the incident radiation. Thermopiles are difficult instruments to use for intensity measurements of radiation with wavelength less than 1000 Å, especially when the radiation is produced by repetitive condensed spark discharges each pulse having approximately a microsecond duration. Since thermopiles are calibrated with a dc light source, the validity of this calibration might be questioned when used with pulsed sources. In the present work, the rare-gas ion chamber method [5] was used to measure the absolute intensity of the incident radiation. This technique is both simple and inherently accurate.

The photoelectric yield is defined here in a practical sense as the number of electrons ejected per <u>incident</u> photon rather than in a more physical sense as the number of electrons ejected per <u>absorbed</u> photon.

EXPERIMENTAL

A 1/2-meter Seya-Namioka vacuum monochromator with a platinized 1200-line/mm grating was used to provide monochromatic radiation between 300 and 1300 Å [6]. The grating was blazed for 600 Å at an angle of incidence of 35° . With 37- μ slit widths, a resolution of 0.7 Å was obtained.

A high voltage repetitive condensed spark discharge in a low pressure gas was used to produce a line spectrum from 1000 to 300 Å. For longer wavelengths, the many lined hydrogen dc light source was used to alleviate the problem of identifying second- and higher-order lines.

Aluminum samples were machined from commercial stock material type 5086-H32. This is an aluminum alloy containing 94 percent $A\ell$ with 4 percent Mg as the major impurity. Minor impurities are; silicon, iron, copper, manganese, chromium, zinc, and titanium. Two samples were studied from different stock material but of the same type, namely, 5086-H32. Sample No. 1 was highly polished on one side and sandblasted on the other side. Sample No. 2 was a cathode from a Bendix type M 306 magnetic electron multiplier. This cathode had a mirror finish.

The photoelectric yield of the first sample had been measured previously [7]. Because of its larger size, this sample was used in the present work to investigate the effect on the yield due to variations of the angle of incidence. Its yield was also measured at discrete wavelengths to check the reproducibility

of the previous calibration. Both samples were cleaned with methyl alcohol prior to any measurements.

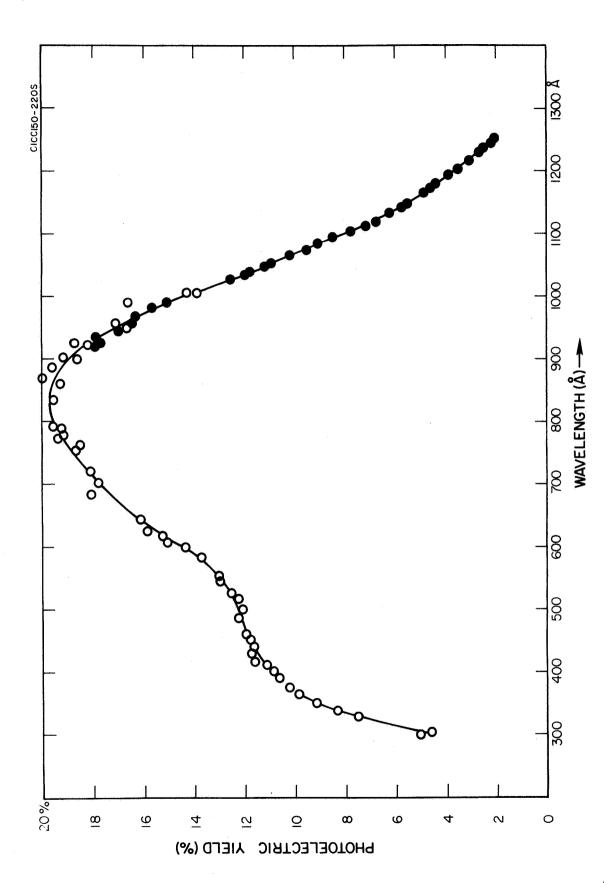
The samples were placed at the end of the rare-gas ion chamber, the other end of which was mounted directly onto the exit slit of the monochromator. At wavelengths below 1022 Å, a suitable rare gas was introduced into the ion chamber and the gas pressure increased until the incident radiation was completely absorbed. Since the photoionization efficiency of the rare gases is 100 percent, the ion current divided by the electronic charge gave the absolute number of photons incident per second on the aluminum. The ion chamber was then evacuated to a pressure of 10⁻⁵ torr and the photoelectric current from the aluminum sample was measured. The voltage used to collect the ejected photoelectrons was increased until all were collected. The ratio of the photoelectric current to the ion chamber current gave the required yield. Departures from linearity or fatigue effects were not observed over the range of illuminating fluxes used in these experiments.

RESULTS

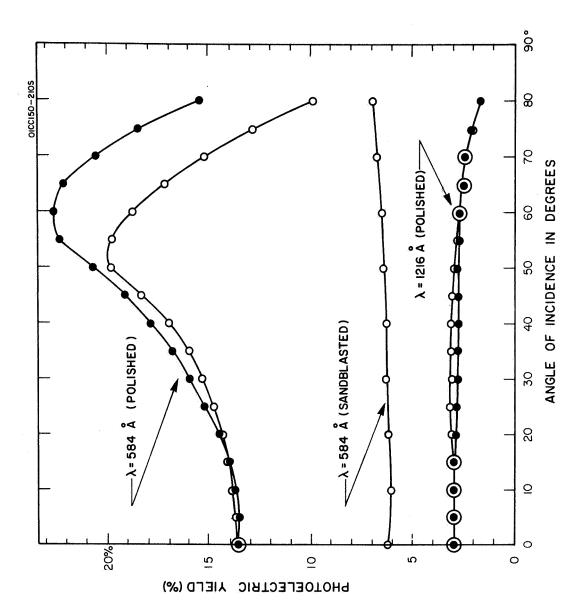
The photoelectric yield of sample No. 2 is presented in Fig. 1. open circles represent measurements made with the rare-gas ion chamber while the solid circles represent data taken relative to a sodium salicylate coated photomultiplier. The data points overlap between 900 and 1000 X enabling the photomultiplier to be calibrated over this wavelength range. The assumption was then made that the sodium salicylate had a constant quantum efficiency at wavelengths between 1000 to 1300 A. There is some evidence that this is so, especially for a fresh coating of salicylate [5,8,9]. If this constancy did not hold, the evidence at present indicates an increase in efficiency towards longer wavelengths [5,9]. At 1250 Å, the efficiency is generally not more than 20 percent greater than that at 1000 A. Hence, although the estimated accuracy of the yield measurements between 400 and 1000 X was ± 8 percent, the error limits at 1250 Å were estimated to be + 20 percent, - 8 percent. Below 400 Å the error limits were approximately ± 20 percent due to the weakness of the incident radiation. Within their respective error limits, the yields of both samples were in good agreement. Further, the yields of sample No. 2 were reproducible after subjecting it to oil contamination and recleaning with methyl alcohol.

Figure 2 presents the photoelectric yield of sample No. 1 as a function of angle of incidence at 584 and 1216 Å. The solid points represent the results obtained by rotation of the sample about a horizontal axis, while the open circles were obtained by rotation about a vertical axis.

The behavior of the 584- and 1216-A lines incident at angles up to 50° on the polished surface was similar to that found by Heroux, et al. [10] for a tungsten cathode. A decrease in yield for angles of incidence greater than 50° was observed in the present data. This decrease was not due to the projected target area of the sample being smaller than the incident beam area since no decrease was observed for the sandblasted side up to angles of 80°.



Photoelectric yield of aluminum as a function of wavelength (sample No. 2). The open circle data points were obtained using the rare gas ion chambers while the solid circle points represent data taken relative to a sodium salicylate coated photomultiplier. Figure 1.



Photoelectric yield of aluminum as a function of angle of incidence (sample No. 1). The open circles represent data for rotations about a vertical axis (i.e., parallel to the exit slit), while the solid circles represent data about a horizontal axis. Figure 2.

Further, the geometry of the experimental arrangement required an angle of incidence of 83° before the projected target area of the sample became equal to the beam area. Thus, the decrease in yield from ≈ 50 to 80° was real. This decrease could probably be ascribed to the high degree of reflectance R at angles of incidence greater than 50° . Since the transmittance is zero, the absorbance must be equal to (1-R). Thus the yield, if defined as the number of electrons ejected per photon absorbed, would be represented by the data in Figure 2 divided by (1-R).

The photoelectric yield at 584 Å was not independent of the axis of rotation, especially for angles of incidence greater than 50°. This could be understood if the 584-X line was partially polarized since the degree of reflectance of polarized light depends on whether the plane of polarization lies in the plane or at right angles to the plane of incidence. Thus it would seem that the 584-X line was partially polarized with its electric vector parallel to the exit slit and to the rulings of the diffraction grating. Partial polarization might be expected for radiation incident upon the grating at any angle other than near normal. In the present case, the angle of incidence was 37° for the 548-A radiation. Further, it is known that diffraction gratings can polarize incident radiation [11]. The 1216-A line, however, appeared to be unpolarized. It is of interest to note that Sasaki and Ishiguro [12], using reflectance techniques with a Seya monochromator, also found the monochromatic radiation to be partially polarized parallel to the grating rulings, the degree of polarization being zero at 1300 Å and increasing towards shorter wavelengths. Their grating was also blazed for 600 Å in the Seya mount.

Sandblasting the surface of the metal had the effect of reducing the yield. This was probably due to the fact that photoelectrons released by radiation penetrating the interstices of the roughened surface had a high probability of being recaptured by the metal. A similar decrease in the yield of gold black compared to a highly reflecting gold surface has also been observed [5]. The calibration presented in Figure 1 is believed to make aluminum type 5086-H32 suitable as a secondary standard in the determination of absolute intensities within the quoted error limits.

ACKNOWLEDGMENTS

The authors would like to express their appreciation to the Bendix Corporation for the sample of the aluminum cathode.



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ENHANCED PHOTOELECTRON EMISSION BETWEEN 200 AND 1300 Å

bу

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ABSTRACT

The photoelectric yield of a metal has been shown to increase with increasing angle of incidence of the radiation. The reflected radiation is reused to cause further photoemission until the incident radiation is entirely absorbed. Using an eighteen sided aluminum polygon to totally absorb the radiation, the photoelectric yield of the polygon compared to that of a single plate used at normal incidence was increased by a factor of 5.5 at 209 Å and by 40 percent at 1216 Å. The yield of the polygon cathode was in excess of 16 percent between 200 and 1000 Å with a maximum yield of 28 percent at 350 Å.

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INTRODUCTION

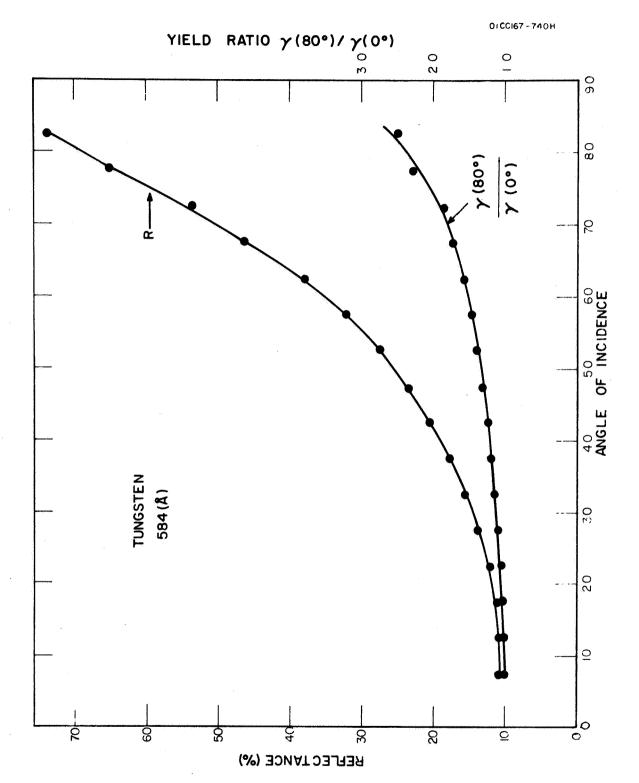
The photoelectric yield of a metal has been shown to increase with the angle of incidence Θ of the radiation. When the yield is defined in the practical sense as the number of electrons ejected divided by the number of incident photons η , the yield increases only to the point where the reflectance is sufficiently high that most of the incident photons are reflected and the yield then drops [1]. When the more fundamental definition is used, namely, the number of electrons ejected divided by the number of absorbed photons γ , it is found that the yield continually increases. Rumsh, et al. [2] have shown this to be true for x rays in the range 1 to 13 A; in fact, when $\Theta \leq 80^{\circ}$, they observed the increase to be proportional to $\sec\Theta$. Heroux, et al. [3] have shown that the increase in γ with Θ also holds in the vacuum uv region, the increase being more rapid as the wavelength decreases. At 304 Å, they showed that the increase in γ was closely proportional to $\sec\Theta$ in agreement with the x-ray data. This agreement may be fortuitous since the x-ray energies ranged from 1 to 12 keV. At these energies, bound electrons from the K and L shells can be ejected whereas at 304 Å (41 eV) the electrons can only be ejected from the conduction band.

The present article describes the utilization of the enhanced emission at grazing angles. The photoemission was increased by a factor of 5.5 at 209 Å while at 1216 Å, the increase was only 40 percent. The experimental apparatus and technique for measuring yields have been described previously [1].

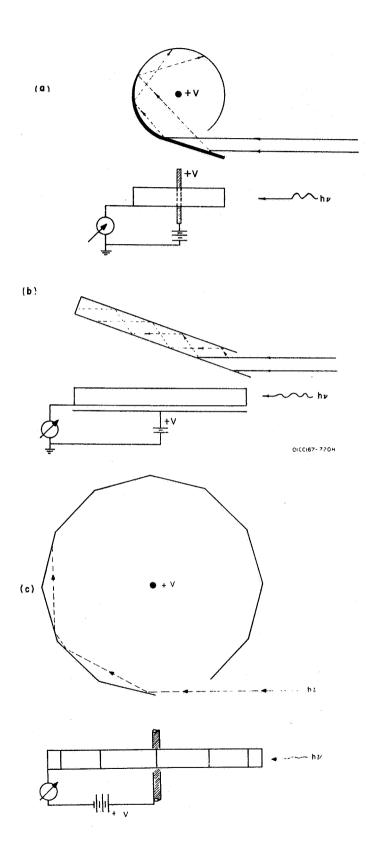
RESULTS

The measurements of Heroux, et al. [3] on the angular dependence of the ratio of the absolute photoelectric yield at an angle of incidence Θ to the absolute yield at normal incidence, $\gamma(\Theta)/\gamma(0^{\circ})$, have been repeated and extended to 82°. Figure 1 shows the yield ratio and the reflectance of tungsten at 584 Å. The yield ratio is in agreement with the data of Heroux, et al. up to 60°, their maximum angle of incidence. At an angle of incidence of 80°, the absolute yield is 2.4 times greater than that at normal incidence while the reflectance is nearly 70 percent. Thus, if the reflected radiation can be directed at 80° onto another sample of tungsten and this process repeated until the radiation has been totally absorbed, the photoelectron emission is increased by a factor of 2.4 relative to the emission at normal incidence.

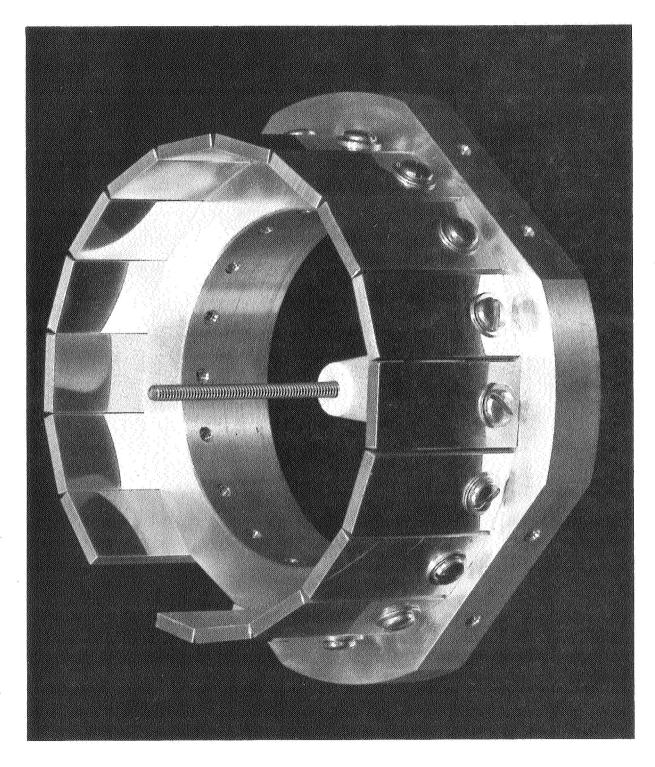
Several experimental arrangements have been tried. These are shown in Figure 2(a), (b), and (c). Using a well collimated beam, increased yields were obtained for each configuration, however, with the cylindrical form [Figure 2(a)] the angle of incidence varies across the width of the beam and the full increase in yield is not obtained. The parallel plate and polygon type cathodes both provided the expected gain in photoelectron emission. The polygon cathode was found to be more compact for numerous reflections. A photograph of an eighteen sided polygon is shown in Figure 3. The sides were made from highly polished aluminum type 5086-H32. The central electrode was



The reflectance of tungsten R and the ratio of the absolute photoelectric yield γ ($\theta^{\rm O}$) at an angle of incidence θ is the yield at normal incidence γ ($\theta^{\rm O}$) measured as a functions of θ at $584 \Re$. Figure 1.

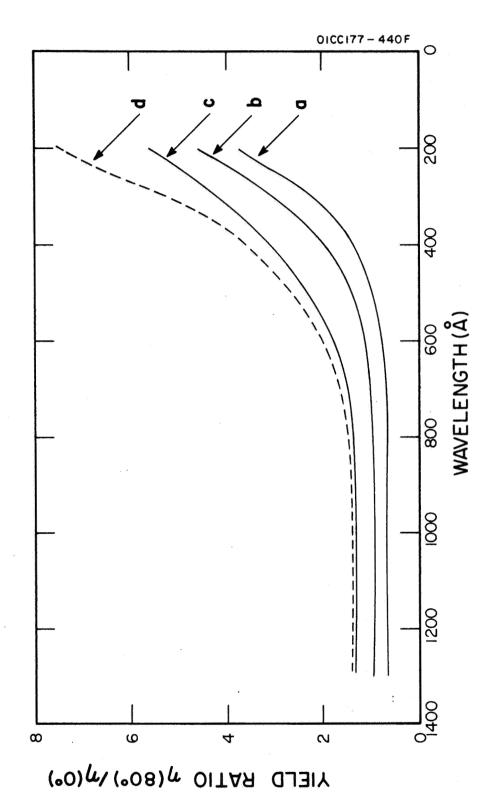


(a) Cylindrical, (b) parallel plate, and (c) polygon cathodes designed to give total absorption of the incident radiation. The positive pin in (a) and (c) can be replaced by a base plate as in (b). Figure 2.

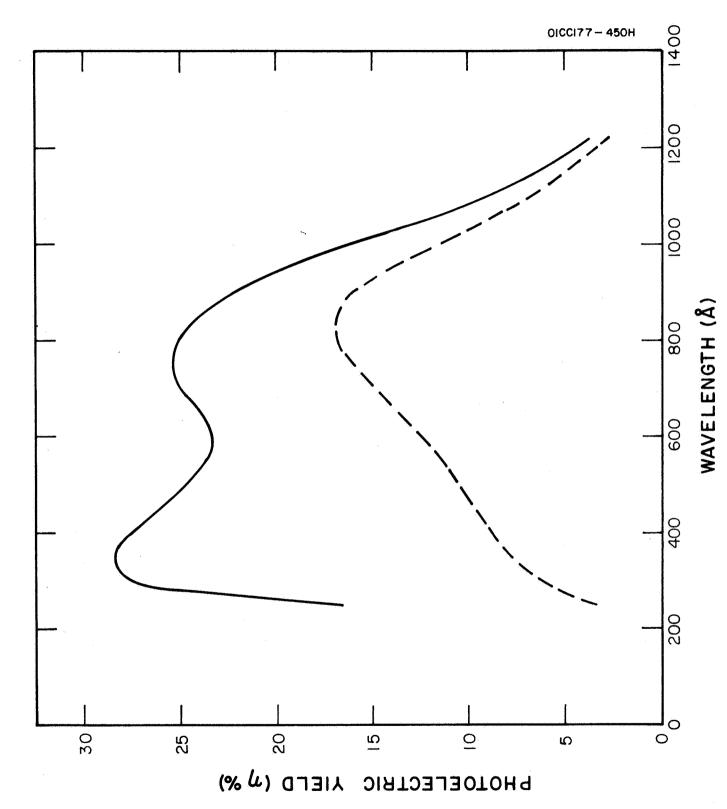


held at approximately + 100 V to collect the electrons. One side of the polygon was removed to allow the radiation to strike the first plate, thus seventeen reflections are obtained at an angle of incidence of 80°. The reflectance of the first plate was measured at 80° and was found to vary between 53 and 66 percent for wavelengths between 1300 and 200 Å. Figure 4 shows the practical yield ratios, $\eta(80^{\circ})/\eta(0^{\circ})$ for the polygon with (a) a single plate, (b) two plates, and (c) for the entire seventeen plates. The dotted curve (d) represents the ratio $\gamma(80^{\circ})/\eta(0^{\circ})$ for a single plate and is obtained from curve (a) by taking into account the reflectance r at 80°, that is, by multiplying curve (a) by 1/(1-r). Since the incident radiation is completely absorbed by the polygon, $\gamma_{\text{poly}}(80^{\circ}) \equiv \eta_{\text{poly}}(80^{\circ})$ and curves (c) and (d) should be identical. This is the case between 1300 and 800 Å, however, the two curves deviate more towards shorter wavelengths. The deviation is probably due to the fact that the radiation from the Seya monochromator becomes progressively more polarized towards the shorter wavelengths. This would particularly alter the reflectance between the first and second plates, the first plate acting as an analyzer and reflecting only one plane of the partially polarized light. Nevertheless, a gain of 5.5 was achieved at 209 X by the polygon with respect to a single plate used at normal incidence. From Figure 4, the gain apparently continues to increase towards shorter wavelengths and, presumably, for greater angles of incidence.

The efficiency of the polygon was not tested with plane polarized light due to the lack of polarizers in this wavelength range, however, it is known that the yield increases with the angle of incidence regardless of the plane of polarization [1]. The photoelectric yield η for the polygon is shown in Figure 5 as a function of wavelength. The yield of a single plate used at normal incidence is shown for comparison. The use of the full number of sides of the polygon is, of course, unnecessary when the reflectance per side is only 60 percent. After ten reflections, 99.4 percent of the incident radiation should be absorbed; however, if the sides are coated with a material of higher reflectance, more sides are needed. The use of a polygon type cathode in conjunction with a windowless electron multiplier should make an excellent detector for the soft x-ray region.



(a) Sin-The photoelectric yield η measured at an angle of incidence of $80^{\rm o}$ relative to that measured at normal incidence, as a function of wavelength. gle plate, (b) double plate, (c) polygon, (d) the ratio γ $(8\tilde{Q}^{\rm o})/\eta$ from curve and (e) taking into account the reflectance at 80° Figure 4.



The photoelectric yield of a polygon cathode (solid line) and a single plate at normal incidence (broken line) measured as a function of wavelength. Figure 5.

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